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Polymer Letters

Editorial Board: R. M. Fuoss · J. J. Hermans · H. Mark · H. W. Melville · C. G. Overberger · G. Smets

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POLYMER LETTERS VOL. 1, PP. 1-5 (1963)

MOLECULAR WEIGHT DEPENDENCE OF ENVIRONMENTAL STRESS CRACKING IN POLYSTYRENE

The mode of fracture of polystyrene has recently been reported to depend somewhat upon the experimental conditions under which the fracture is induced (1). It is the purpose of this communication to present data which points to the importance of molecular weight parameters in the fracture process.

During the course of an investigation of the effect of molecular weight distribution on the orientability of polystyrene (2) it was observed that the higher molecular weight polymers exhibited a crack pattern, when subjected to a sudden tensile load and held at a fixed elongation, which was decidedly different from that obtained with lower molecular weight materials. In the former case the cracks produced were much more numerous than in case of the latter; in addition, the cracks ran uniformly in a direction perpendicular to the direction of stretch (Fig. 1). These observations were interpreted as indicating that the materials which were made up of predominantly long chain molecules exhibited more gradual stress release than those in which such molecules were lacking and that, in the former, stress release was less likely to be accompanied by catastrophic failure.

To verify this, resistance to environmental stress cracking was measured on five narrow distribution (anionically polymerized) polystyrenes in the presence of a stress crack reagent which produced failure in a reasonable length of time (n-butanol). Five broad distribution (isothermally polymerized) polystyrenes were used as comparison materials, molecular weights and heterogeneity indices of all the polystyrenes be-

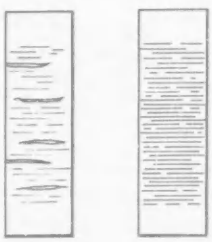

Fig. 1. (a) Cracking pattern in low molecular weight polystyrene. (b) Cracking pattern in higher molecular weight polystyrene.

TABLE I

Polystyrene Samples

Material	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	H.D., °C	τ_{av}, sec. (σ_0 = 1000 p.s.i.)
		Anionic Polystyrene		
S103	124,700	1.05	103	38.0
S105	153,500	1.04	101	148
S109	193,000	1.06	102	8,300
S111	239,000	1.08	100	24,300
S108	267,000	1.08	105	169,500
		Isothermal Polystyrene		
B2	187,000	1.90	97	95.3
B3	214,000	1.94	96	1,700
B4	255,000	1.96	100	7,700
B5	285,900	1.77	100	53,900
B6	447,000	2.85	97	268,000

ing listed in Table I. Measurements were made at room temperature (26 ± 1°C.) using a "square doughnut" relaxometer which has been developed at M.I.T. (3).

An initial tensile stress of 1,000 p.s.i. (corresponding to a strain of 0.22%) was applied to the specimen under examination and stress crack reagent allowed to moisten a small piece of blotting paper affixed to the

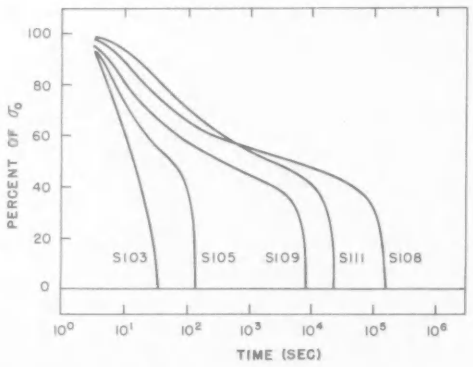

Fig. 2. Stress decay curves for narrow distribution (anionic) polystyrenes in butanol environment. σ_0 = 1000 p.s.i.

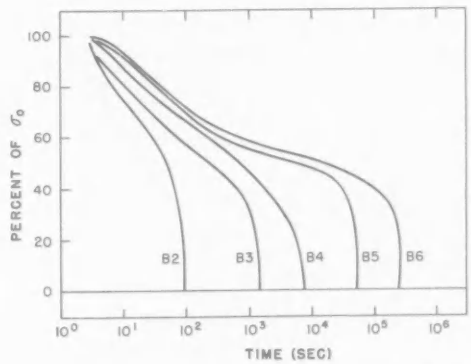

Fig. 3. Stress decay curves for broad distribution (isothermal) polystyrenes in butanol environment. σ_0 = 1000 p.s.i.

specimen surface. The stress decay which ensued was transmitted through a weighbar consisting of two resistance-type strain gages cemented to opposite sides of a piece of spring steel and this decay then recorded on a Minneapolis-Honeywell strain recorder. Stresses were obtained knowing the calibration curve for the particular strain gages used and the dimensions of the test specimen. Stress decay was followed until failure occurred or until a condition of total relaxation was reached.

Typical stress decay curves for all the materials tested are shown plotted in Figures 2 and 3 as per cent of initial stress (σ_0) vs. log time. It will be noticed that the decay rates for both the broad and the narrow distribution polymers show a uniform decrease with increasing molecular weight. In addition, there appears to be a tendency for the decay curves to form a shoulder or gently sloping plateau before dropping to zero stress as molecular weight increases.

If the average times at which the stress reaches zero (t_{av}), whether this occurs in a catastrophic fashion or by a more gradual relaxation process, be plotted logarithmically against molecular weight, as is done in Figure 4, the molecular weight dependence of stress cracking is clearly seen. The solid and open points in this figure are averages of from three to five determinations while the vertical lines represent the extent of experimental scatter.

Reduced resistance to stress crazing at low molecular weights has sometimes been attributed to the existence of voids and imperfections due to end groups (4). Such an explanation can obviously not be employed in the case of the narrow distribution polystyrenes used here since these have been shown both by sedimentation analysis and by chromatographic fractionation (5) to be lacking in molecular components smaller than M = 75,000. The high heat distortion values of the anionic

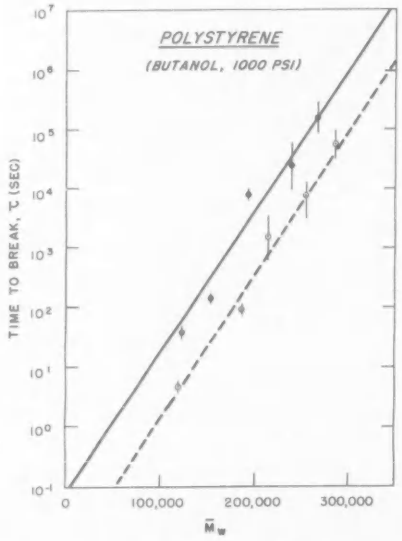

Fig. 4. Dependence of time to break upon $\bar{M}_w$ for polystyrene in butanol environment. σ_0 = 1000 p.s.i. (Solid points are narrow, open circles are broad distribution polystyrene.)

polystyrenes listed in Table I underline this absence of short chain molecules.

The foregoing should not be interpreted to mean that test specimens prepared from anionic materials are completely lacking in macroscopic imperfections. It is probable that all test specimens, no matter how carefully prepared, contain a certain number of flaws, voids, etc., which can act as stress concentrators (although it has recently been pointed out that such flaws do not necessarily have to pre-exist in a polymer to be effective crack initiators (1,6)).

The observed relationships between time to fail, relaxation rate and molecular weight suggest that the events antecedent to catastrophic failure are dependent in some way upon intermediate range molecular motions (chain uncoiling vs. chain slippage). Tentatively, we may say that long chain molecules tend to hamper crack propagation in at least two ways: By absorbing energy from the growing crack tip and by restraining the separation of fracture surfaces until the chains have uncoiled completely and carbon-carbon bond rupture takes place. In the limiting case of a very long molecule the time and stress required for the accomplishment of uncoiling would be so great as to make bond rupture the preferred mechanism.

The possibility that solvent absorption is controlled by molecular weight has been checked superficially over the molecular weight range studied here using conventional absorption techniques; to date, however, no positive results have been obtained.

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STRESS CHANGES IN A STRETCHED VULCANIZATE DUE TO GEOMETRIC ISOMERIZATION ABOUT DOUBLE BONDS IN THE POLYMER CHAIN

Changes in stress, induced by chemical agencies, in an extended elastomer vulcanizate at a constant temperature are usually attributed to the introduction, removal, or rearrangement of crosslinks or to scission of the polymer main chain. We have shown that quite large changes in stress can occur when the causes enumerated above are suppressed or their effects eliminated, the only change occurring in the network being that of molecular geometry about double bonds in the polymer chain.

Polyisoprenes undergo isomerization at the double bonds by an "on-off" reaction with sulfur dioxide at elevated temperatures to give an equilibrium polymer with a cis to trans ratio of about 1 to 3 (1).

Continuous stress relaxation measurements were made, in an atmosphere of 700 mm. sulfur dioxide at 100°C. (Fig. 1), on ethyl acetate extracted dicumyl peroxide vulcanizates of natural rubber, gutta percha, and synthetic cis polyisoprene as part of an investigation into the effect of isomerization on the physical properties of vulcanizates (2). The relaxation measurements were made with the vulcanizates extended by 100% in an automatic stress relaxometer (3). Where increments of stress were observed the relaxometer was modified so as to operate in the reverse direction to that described.

Natural rubber and cis polyisoprene showed a drop in stress of 30% compared with a drop of 5% in nitrogen or vacuum. The stress drop in a peroxide vulcanizate in an inert atmosphere is due to scission of the main chain at pre-oxidized sites and probably still occurs in sulfur dioxide.

Natural rubber which had been isomerized in sulfur dioxide at 100°C. for 70 hrs. (so that the cis to trans ratio was approaching the equilibrium value) and then cured, showed a drop in stress of about 10%.

Gutta percha shows an increase in stress of up to 10%.

The drop in stress observed with rubber in sulfur dioxide cannot be due entirely to chain or crosslink scission induced by the sulfur dioxide for then the stress would be expected to decay to zero (unless it is assumed there are certain sites on the polymer which are preferentially attacked).

No theory involving scission can explain the gutta results, and therefore it is unlikely that the effect observed in rubber is due to scission either.

The kinetics of these stress changes run parallel to the kinetics of the isomerization reaction as determined from changes in the infrared

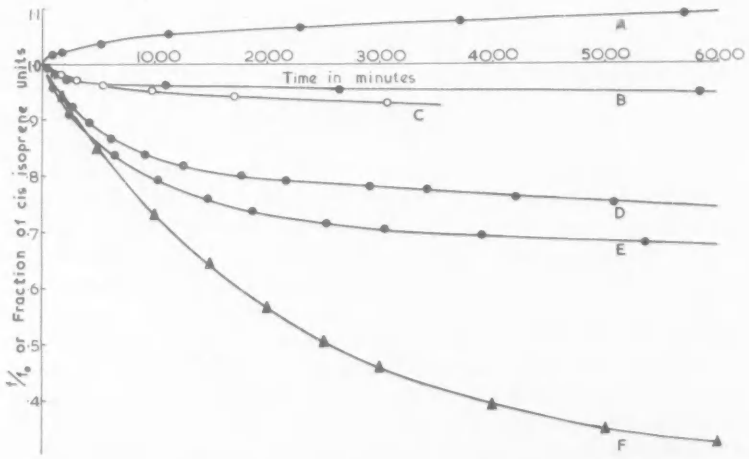

Fig. 1. Stress relaxation of (A) gutta percha in SO_2 at 100°C., (B) natural rubber in N_2 at 100°C., (C) isomerized natural rubber in SO_2 at 100°C., (D) cis polyisoprene in SO_2 at 100°C., and (E) natural rubber in SO_2 at 100°C. Curve F: fraction of cis isoprene units in natural rubber in SO_2 at 100°C.

spectrum of the polymer. It is not possible to construct a precise relationship between stress change and isomerization because of uncertainties in the kinetic measurements and the elasticity theory. The magnitude of the ratio of the decrement in stress in rubber to the increment in stress in gutta is of the same order as the equilibrium cis to trans ratio.

The simple extension stress strain relation given by the statistical theory of rubber elasticity may be written in the form

$$f = NkT\beta(\lambda - \lambda^{-2}) \tag{1}$$

where f is the stress referred to the unstrained cross-section, λ the extension ratio, N the number of molecular chains between crosslinks per unit volume, T the absolute temperature, and k Boltzmann's constant. The factor β is given by

$$\beta = r_0^2 n^{-1} l^{-2} \tag{2}$$

where n is the number of random links each of length l in a molecular chain and r_0 the root-mean-square distance between the ends of a chain in the unstrained state (4-6). For a vulcanizate crosslinked in the dry state it is usually assumed that r_0 is given by the dimensions of a free

unrestrained chain of appropriate n and l values. In this case r_0 is equal to $ln^{1/2}$ so that β is unity and the stress strain relation (1) is independent of the size of the random link. If, however, the size of the random link is altered subsequent to the introduction of crosslinks, r_0 will no longer be equal to $ln^{1/2}$ as the crosslinks cannot move, but will remain constant although n and l change. The contour length L of the chain will be unaltered by isomerization of the double bonds so that

$$L = nl \tag{3}$$

and eq. (2) becomes

$$\beta = r_0^2 L^{-1} l^{-1} \tag{4}$$

Substitution of this value of β in eq. (1) gives

$$f = NkT(\lambda - \lambda^{-2}) r_0^2 L^{-1} l^{-1}$$

The stress f at a given strain will therefore be inversely proportional to the size of the random link if this is altered after the introduction of the crosslinks.

The absolute values of l for the cis and trans forms of polyisoprene are open to doubt, but l cis is the smaller being about two-thirds of l trans (4,7). Therefore isomerization of an all-cis polyisoprene vulcanizate in a stretched state should result in a relaxation of stress and isomerization of an all-trans vulcanizate in an enhancement of stress as observed.

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FORMAL ANALOGY BETWEEN THE COPOLYMERIZATION Q-e SCHEME AND THE HAMMETT EQUATION

Some years ago, a semi-quantitative relationship in copolymerization was proposed by Alfrey and Price (1) in which the monomer reactivity ratios could be calculated by the two parameters Q and e characteristic of the monomers. The relative rates at which monomers 1 and 2 compete for radicals were shown to be

$$r_1 = k_{11}/k_{12} = (Q_1/Q_2) \exp\{-e_1(e_1 - e_2)\} \quad (1)$$

$$r_2 = k_{22}/k_{21} = (Q_2/Q_1) \exp\{-e_2(e_2 - e_1)\} \quad (2)$$

where Q_1 and Q_2 are the mean reactivities of the monomers (determined by the resonance effect); and e_1 and e_2 are the polar factors which are proportional to the residual electrostatic charges in the respective reacting groups.

Despite the essentially empirical character of their original derivation, the considerable success these ingenious equations have achieved over the years warrants their validity. Rigorous theoretical justifications are still not available at the present time. Here we wish to point out an interesting formal analogy between the Alfrey-Price equation and the well-known equation in organic chemistry: the Hammett equation.

It was proposed by Hammett (2) in 1935 that the effect of meta and para substituents in the benzene ring on reaction rates and equilibria in many polar reactions could be expressed by the following equation:

$$\log (k/k_0) = \rho\sigma \quad (3)$$

where k and k_0 are the rate or equilibrium constants for the substituted and unsubstituted phenyl compounds, σ is a measure of the ability of the substituent to change the electron density at the reaction center, and ρ is the reaction constant which measures the sensitivity of the equilibrium in question to a change in electron density. In this equation, however, the resonance effect is not taken into account. Taft (3) pointed out that the polar effect of the substituent and the resonance effect of the functional group are independent variables. The substituent effect on rate or equilibrium is therefore a composite function of polar and resonance effects. He modified the Hammett equation in the following manner:

$$\log (k/k_0) = \rho\sigma + R \quad (4)$$

The R value is the total effect on the $\log (k/k_0)$ value resulting from

resonance interactions. If one now regards the copolymerization reaction kinetics as one that follows the Hammett-type relationship, and redefines the corresponding parameters:

$$\ln (k_{11}/k_{10}) = \rho_1' \sigma_1' + \ln q_1 \tag{5}$$

Here k_{11} is the rate constant for monomer 1 to homo-polymerize with a monomer of its own type, whereas k_{10} is that with an unsubstituted phenyl-type monomer, say styrene. R is written into logarithmic form for reasons soon to be obvious. Similarly,

$$\ln (k_{12}/k_{10}) = \rho_2' \sigma_2' + \ln q_2 \tag{6}$$

where k_{12} is the rate constant for monomer 1 to copolymerize with monomer 2. Subtract eq. (6) from eq. (5) and rearrange:

$$r_1 = k_{11}/k_{12} = (q_1/q_2) \exp \{\rho'(\sigma_1' - \sigma_2')\} \tag{7}$$

where $\rho' = \rho_1' = \rho_2'$, since they are the reaction constants for the same reaction. Similar derivation will yield:

$$r_2 = k_{22}/k_{21} = (q_2/q_1) \exp \{\rho'(\sigma_2' - \sigma_1')\} \tag{8}$$

When unsubstituted monomers are involved, q_0 can be considered to be one, and σ_0 zero. The striking resemblance of eqs. (7) and (8) to eqs. (1) and (2) is immediately evident. On the right-hand sides of all these equations, the pre-exponential factors account for the resonance effects and the exponentials themselves are responsible for polar effects. The sign difference and the presence of one more parameter in $\{\rho'(\sigma_1' - \sigma_2')\}$ in comparison with $\{-e_1(e_1 - e_2)\}$ should not affect the theoretical soundness of the analogy. Certainly the analogy is not exact, since these parameters have their own arbitrarily defined values. However, it is tempting to conclude that the Hammett and Alfrey-Price equations may have the same theoretical basis. Therefore, the Copolymerization Q-e Scheme could probably be justified by linear free-energy relationship arguments, at least for the aromatic monomers.

A number of authors have long before observed the similarity between these two equations (4,5). Linear relationships have been demonstrated to exist for their respective parameters. The formal analogy given in this communication renders their correlation more complete. These relationships were originally derived for radical-initiated copolymerizations. Recently, Tobolsky and Boudreau (6) found good agreement in correlating for ionic-initiated copolymerizations. This indicates that the analogy is of a rather general nature.

The author wishes to thank Prof. A. V. Tobolsky and Dr. T. Alfrey for their interest and valuable discussions.

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POLYMER LETTERS VOL. 1, PP. 15-17 (1963)

FRACTIONAL PRECIPITATION OF POLYACRYLONITRILE

The choice of a solvent-precipitant system is very important for the fractionation of polymer because the effectiveness of fractionation greatly depends upon the system. Various solvent-precipitant systems have been proposed for the fractionation of polyacrylonitrile which have some merits and disadvantages at the same time. For instance, high temperatures are needed for the dimethylformamide-heptane system (1) because of poor solubility of heptane in dimethylformamide, and in the dimethylformamide-heptane-ether system (2) the precipitated polymer fractions easily form colloidal particles. For the nitric acid-butyl alcohol system (3) a lower polymer concentration is needed to obtain the comparable effectiveness in fractionation to those of other systems (4). The stability of solvents is not good enough in the hydroxy acetonitrile-benzene-ethyl alcohol system (5).

A number of experiments on fractionation were carried out and we came to the conclusion that the dimethylsulfoxide-toluene system is the easiest to handle and its effectiveness of fractionation is very good. The details of this method are described below.

Hydrogen chloride-containing dimethylsulfoxide (6-8 cc. N-HCl in 100 cc. dimethylsulfoxide) was used as the solvent. The reason why hydrogen chloride was added was to prevent the coloration of polymer solution and to improve the effectiveness of fractionation. Toluene was slowly added through a capillary into the well-stirred polymer solution at 35°C., and the usual fractional precipitation method was used. In this case, the gel phase was very transparent and little skill is needed to see approximately how much polymer separates as the gel phase. The gel phase usually adheres to the bottom of the flask like mud and can be easily separated by decantation. To improve the effectiveness of fractionation, we often use the simple technique by which the separated gel phase is treated for 30–60 min. at 35°C. with a solvent-precipitant mixture which has almost the same composition as that of the dilute phase. To extract lower molecular weight polymer species in the gel phase by this treatment makes the fractionation more effective than by the usual method which involves re-dissolving the gel after the onset of phase separation by raising the temperature a few degrees, and then lowering the temperature again to 35°C. to separate the fraction in favorable circumstance. The separated gel phase was then dissolved in dimethylformamide (or dimethylsulfoxide) and the solution was poured into ethyl alcohol or water to reprecipitate the polymer. It is advisable not to add ethyl alcohol or water directly to the separated gel phase because it creates a very hard block which is difficult to crush.

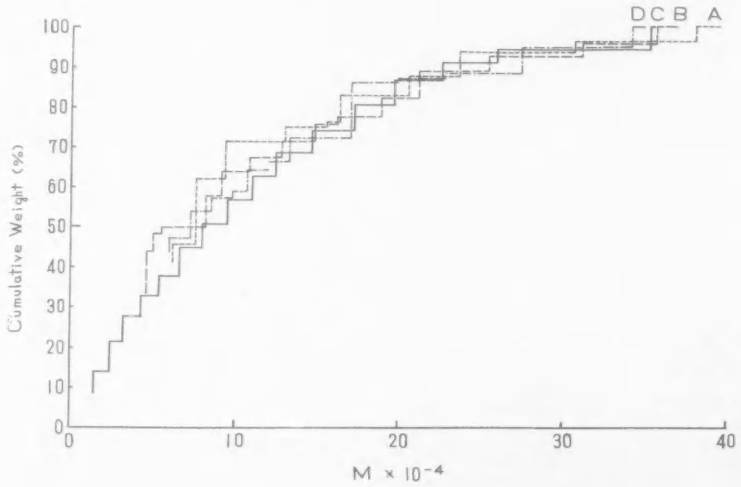

Fig. 1. Effect of adding acids on fractionation by dimethylsulfoxide-toluene system. Initial polymer concentration, 0.6 g./100 cc. Acid added: $(COOH)_2$ on curve B, HCl on curve C, and H_3PO_4 on curve D. Curve A represents a blank.

As mentioned above, some hydrochloric acid was added to the system to improve the effectiveness of fractionation. The effects of acids added are shown in Figure 1, where the cumulative weight (%) is plotted against molecular weight. Molecular weights in the figure were obtained from viscosity measurement of dilute polymer solution in dimethylformamide at 35°C., and were calculated according to the following equation (6):

$$[\eta] = 2.78 \times 10^{-4} M^{0.76}$$

In Figure 1, A is the case where we did not add an acid, but oxalic acid was added in case B, hydrochloric acid in case C, and phosphoric acid in case D, so that pH's of 25% aqueous solutions were adjusted to be 3. As is clearly seen in this figure, fractionation was conveniently carried out with the addition of hydrochloric acid, but in the other cases the precipitate became colloidal which made it impossible to separate the system. In case C, where hydrochloric acid was added, the last polymer fraction, 8.2% of the initial amount, was obtained by drying the polymer solution which gave no more precipitate on further addition of precipitant, and it was 40.9% in case A, 32.4% in case B, and 44.1% in case D. Most of the last polymer fractions thus obtained in cases A, B, and D derived from the colloidal particles which could not be separated by

centrifugation of 3000 g. These last fractions are not shown in Figure 1. In such a case where a part of the phase-separated polymer becomes colloidal, the volume fraction of polymer in the gel phase is small compared to the other systems, which causes the poor effectiveness of fractionation. This problem will be discussed in detail in another paper.

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THE MEASUREMENT OF DIFFUSION CONSTANTS OF GASES IN POLYMERS BY SORPTION TECHNIQUES

Introduction

The determination of gas diffusion constants in polymers can provide information on polymer morphology (1-4) and data on the separation effectiveness of membranes. The most versatile technique for measuring these coefficients is the Barrer time-lag method (5). However, situations are sometimes encountered where the method cannot be used effectively, due to low diffusion constants in a given polymer system. Examples are sulfur hexafluoride in polyethylene and methane in polyethylene terephthalate. In these instances, the time-lags in the thinnest available membranes are impractically long and even small leak rates become important.

To overcome these obstacles, sorption techniques have been developed in this laboratory. The experiments may be as much as 40% shorter than the corresponding time-lag experiments and the effects of small leaks can be made negligible.

The method described herein corresponds to sorption by a plane sheet immersed in a limited volume of solute, and was applied to the measurement of diffusion constants of carbon dioxide and methane in polyethylene terephtalate. Alternatively, sulfur hexafluoride diffusion constants in polyethylene were measured by following the desorption of the gas from essentially infinite cylinders into a limited volume (6). These methods may be applied when the gas solubility is sufficiently high to assure a readily measurable pressure change in the course of the experiment (>30 mm. Hg).

Lundberg, Wilk, and Huyett (7) have recently reported sorption experiments carried out with molten polymers confined under high pressure in cylindrical vessels. The principal difficulty arose in the estimation of the initial pressure, since gas diffusion constants are large (10^{-5} to 10^{-6} cm.^{2}/sec.) in the molten polymers and the initial pressure drop is very rapid. A trial and error technique, with the aid of a computer, was employed to obtain the best fit of the data, plotted in the form of a solution to the Fourier equation appropriate to the chosen geometry and operating conditions.

In contrast, since the diffusion constants of carbon dioxide and methane in polyethylene terephthalate are quite low (10^{-9} to 10^{-10} cm.^{2}/sec.), the initial pressure could be determined accurately from an extrapolation of data taken early in a run and there was no need for a trial and error procedure in this work.

Experimental

Cells were designed to admit rolls of polymer film leaving a minimum of void space. The ratio, (polymer volume/void volume), was about 1/3. Plane sheet geometry was attained by coiling sheets of the polymer with a "spacer" approximately 5 mm. wide and 0.125 mm. thick. The cells were standard 71/60 ground glass joints closed off at the bottom. They were inserted into a high vacuum system connected to a manometer. The cell volume was made large compared to the auxiliary ambient volume (feed lines, etc.) and the cell was immersed in a constant temperature bath, controlled to ±0.1°C. After evacuation of the sample, gas was admitted to the apparatus and the rate of pressure fall was monitored either directly with a cathetometer or indirectly, as a voltage change, on a recorder. The manometer was of the usual mercury type, except that a platinum wire was inserted into one leg, through which a constant current was passed. As the height of mercury in the leg changed, the electrical resistance of the leg increased and the potential drop (in millivolts) increased. This potential drop was traced on the recorder, and later converted to pressure.

For the case of sorption by a plane sheet immersed in a limited volume of solute, Crank (8) gives the solution for the fractional equilibration, $\bar{E}$, as a function of time.

$$\bar{E} = 1 - \sum_{n=1}^{\infty} \frac{2\psi(1+\psi)}{1+\psi+\psi^2 q_n^2} \exp\{-4Dq_n^2 t/L^2\} \qquad (1)$$

In eq. (1), D is the diffusion constant in cm.^{2}/sec., t is time in seconds, and L is film thickness in cm. The quantity ψ is the ratio of initial pressure to total pressure drop (initial pressure minus final pressure).

$$\psi = p_i/(p_i - p_f) \qquad (2)$$

For very short times, $\bar{E}$, which equals $(p_i - p_f)/(p_i - p_f)$, is linearly related to the square root of the dimensionless group Dt/L^2, as shown by Crank (8). Therefore, for gases with low diffusivities (10^{-9} to 10^{-10} cm.^{2}/sec.), the initial pressure may be determined with neglibible error by extrapolating a plot of p vs. $\sqrt{t}$ to zero time. However, for systems in which the diffusion constant is large (10^{-5} to 10^{-6} cm.^{2}/sec.) this extrapolation cannot be satisfactorily performed, since the pressure drop is initially very rapid.

At sufficiently long times, only the first term of the series is important and eq. (1) may be rearranged to

$$1 - \bar{E} = \frac{p - p_f}{p_i - p_f} = \frac{24(1+\psi)}{1+\psi+\psi^2 q_1^2} \exp\{-4Dq_1^2 t/L^2\} \qquad (3)$$

where p is the pressure at time t, and q is a solution of the transcendental equation

$$\tan q_n = -\psi q_n \tag{4}$$

and is tabulated by Crank (8). When $1 - \bar{E}$ is smaller than 0.3, neglecting the higher order terms introduces an error of less than 2%.

The diffusion constant is obtained from the slope of a semi-logarithmic plot of eq. (3), since

$$D = \frac{L^2}{\psi q_1^2} \cdot \frac{1}{t_{0.1}} \ln (10Z) \tag{5}$$

Here the coefficient $24 (1 + \psi)/(1 + \psi + \psi^2 q_1^2)$ is replaced by Z and the time corresponding to $1 - \bar{E}0.1$ by $t_{0.1}$.

Results

A typical plot appears in Figure 1. Evidence for the correctness of the assumption of plane sheet geometry is the agreement between experimental and calculated values of the intercept (0.77). The linear portion

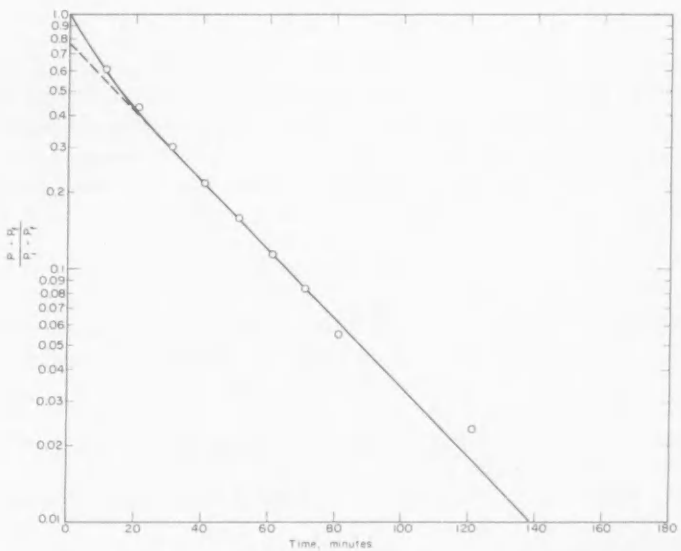

Fig. 1. Plot of experimental data for determination of diffusion constant; (o) run 35S, CO_2 at 75°C. in polyethylene terephthalate ($\alpha = 0.57$).

of the curve commences near $1 - \bar{E} = 0.3$, as expected. The precision limits on D by this method are estimated at ±8% at the 95% confidence level for amorphous films, where thickness variations can be minimized. The precision limits are about ±16% for crystalline films of polyethylene terephthalate, where thickness variations were more pronounced. The data obtained by this method are listed in Table I.

Table I

Gas Diffusion Constants in Polyethylene Terephthalate

Gas	α^*	T (°C.)	D (cm.^{2}/sec.)
CO_2	0.57	55	3.29×10^{-9}
CO_2	0.57	65	5.96×10^{-9}
CO_2	0.57	75	9.56×10^{-9}
CH_4	1.0	45	1.17×10^{-9}
CH_4	1.0	64	3.35×10^{-9}
CH_4	0.57	50	8.30×10^{-10}
CH_4	0.57	65	2.01×10^{-9}

*α is the amorphous volume fraction obtained from density measurements at 25°C.

Conclusions

Sorption techniques can be used for the measurement of diffusion constants of gases in polymers, when diffusivities are too low ($<10^{-9}$ cm.^{2}/sec.) for time-lag measurements. For gases with diffusion constants in the intermediate range (10^{-7} to 10^{-9} cm.^{2}/sec.) such methods may also be used to determine these constants for comparison with those determined by the time-lag method.

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POLYMERIZATION OF TOLYLENE-2,4-DIISOCYANATE

It has been found that when tolylene-2,4-diisocyanate (TDI) is heated in air, oxygen, nitrogen, or exposed to ultraviolet radiation, it polymerizes to give linear polymers of different molecular weights according to the experimental conditions. The diisocyanate turns yellow then dark brown on prolonged heat treatment; under ultraviolet radiation, a dark yellow color is obtained after 2 hr.

Pyrolysis of TDI in dry air at 130° from 4 to 10 days gave low molecular weight polymers up to the heptamer as judged by molecular weight measurements and elemental analysis.

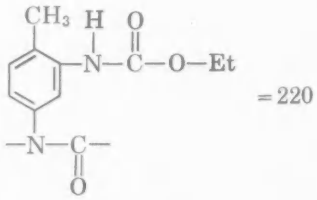
The method of isolation was to remove the excess TDI under reduced pressure at 99-100°C. The residue remaining was reacted with an excess of absolute ethanol to give the polymeric ethylcarbamates. These were fractionally crystallized from ethanol to give the cyclic dimer; m.p. 216-217°C., which is insoluble. The linear polymers were obtained using chloroform and ether to give white or light yellow polymers.

Fraction	M.p., °C.	MW (Rast method) camphor	MW (ebulliometric method) solvent $CHCl_3$
1	116-125	402	424
2	153-163	800	782
3	177-187	2113	1470

Elemental analysis for fraction 2 calculated as a tetramer:

	C	H	N
Calc.	59.61	5.72	12.09
Found	59.54	5.51	12.03
	59.28	5.37	12.15

Those fractions possessed the following characteristics: identical infrared spectrum, lack of sharpness of absorption peaks, failure to recrystallize or sublime, and different softening points. Those data showed that the products were polymers, the structural unit of which was



$= 220$

At 150-160° after 250 hr., the dissocyanate became a deep yellow solid containing about 10% of polycarbodiimide measured by the amount of CO_2 evolved. Treatment of this polymer with an excess of ethanol gave a yellow polymer which did not melt up to 290°C. Beside a shoulder at 4.4 μ characteristic of carbodiimide function, the infrared spectrum of the compound was identical to those obtained in the pyrolysis of TDI at 130°C.

The structure of those polymers was finally confirmed by comparison with the (ethylcarbamate) of the linear polymer obtained by anionic polymerization according to Shashoua's procedure (2,3). This has shown for the first time that it is possible to obtain homopolymers by thermal or radiation polymerization.

The authors are grateful to the National Lead Company for generous support of this work.

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PREPARATION OF SYNDIOTACTIC POLYMETHACRYLIC ACID

In a previous communication (1) we reported the preparation of isotactic polymethacrylic acid by hydrolysis of isotactic polymethyl methacrylate in 96% H_2SO_4 at 60°C. Attempts to prepare the syndiotactic polyacid by hydrolysis of syndiotactic polymethyl methacrylate were unsuccessful. The syndiotactic polyester dissolves as readily in concentrated sulfuric acid but the polymer recovered upon precipitation in water contains a considerable quantity (over 20%) of unhydrolyzed ester groups. The same results were obtained at higher temperatures and H_2SO_4 concentrations approaching conditions under which the polymer is charred.

We have succeeded in preparing highly syndiotactic polymethacrylic acid by polymerization of methacrylic acid at Dry-Ice temperature. One volume of glacial methacrylic acid (Rohm and Haas Co., Philadelphia, Pa.) freed of inhibitor (N,N-diphenyl paraphenylenediamine) by vacuum distillation, was dissolved in two volumes of dry methanol. The mixture was outgassed by twice freezing in liquid nitrogen and evacuating and was finally sealed off under vacuum. After warming briefly to about 0°C. to completely melt and dissolve the monomer, the ampule was cooled to Dry-Ice temperature (the monomer remains in solution) and irradiated for a total dose of 7.1 megarads in a cobalt 60 gamma ray source of 0.16 megarads/hr. The resulting viscous, slightly hazy mixture was poured into hexane. The precipitated polyacid (yield about 35%) was vacuum dried and methylated with diazomethane in benzene according to the method of Katchalsky and Eisenberg (2). The benzene solution of polymethyl methacrylate was filtered, precipitated in hexane and vacuum dried at 60°C.

The tacticity was deduced from the NMR spectrum (Varian 60 Mc/s spectrometer with heated probe) of a chloroform solution of the polymethyl methacrylate according to the method of Bovey and Tiers (3). The value obtained by measurement of the area under the syndiotactic alpha methyl peak showed 85% syndiotactic triads.

A sample of "ordinary" polymethacrylic acid prepared by azobisisobutyronitrile initiation in methyl ethyl ketone at 60°C. and methylated as described above was found to be 57% syndiotactic.

Assuming that in both cases the propagation is governed by a single sigma value as defined by Bovey and Tiers (3) and given by $\sigma = 1 - s^{1/2}$ where s is the fraction of syndiotactic triads, we calculate $\sigma = 0.079$ and 0.245 at –78 and 60°C. respectively. In both cases the single sigma assumption appears justifiable on the basis of (less accurate) measurements of the smaller heterotactic and isotactic alpha-methyl peak areas.

Overlooking the differences in solvent and mode of initiation, these data may be used to estimate the difference in enthalpy and entropy of activation for isotactic and syndiotactic monomer placement given by

$$\Delta(\Delta H_p^{\ddagger}) = \Delta H_i^{\ddagger} - \Delta H_s^{\ddagger} = -R\partial \ln [\sigma/1 - \sigma]/\partial(1/T)$$
$$= 1.2 \text{ kcal./mole}$$

and

$$\Delta(\Delta S_p^{\ddagger}) = \Delta S_i^{\ddagger} - \Delta S_s^{\ddagger} = R \ln [\sigma/1 - \sigma] + \Delta(\Delta H_p^{\ddagger})/T$$
$$= 1.5 \text{ e.u.}$$

Both of these parameters are greater than the values found by Bovey (4) for methyl methacrylate. The differences indicate that the activated complex for isotactic placement is more loosely bonded and energetically unfavorable relative to syndiotactic placement in methacrylic acid than in methyl methacrylate polymerization.

This investigation was supported in part by a Predoctoral Fellowship (No. GF-11, 527-C1) from the Division of General Medical Sciences, Public Health Service.

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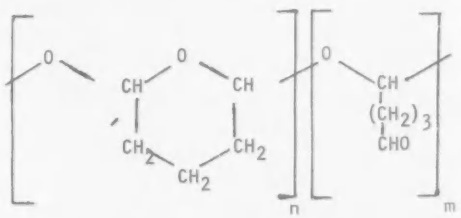
LINEAR POLYGLUTARALDEHYDE

The polymerization of aldehydes has received considerable attention within recent years. A review of the developments in this field has recently been made by Bevington (1). The work to date has involved almost exclusively the polymerization of monoaldehydes. There are scattered reports in the older literature of polymers of dialdehydes (2,3) but no detailed examination of the polymerization reactions or the structure and properties of the polymers has been made. In the polymerization of nonconjugated dialdehydes one would predict, as Bevington did (1), that the aldehyde units would react independently giving crosslinked polymers.

The principle first discovered by Butler (4) in 1957 that certain nonconjugated diolefins may be polymerized by an alternating intra-intermolecular propagation mechanism to produce linear, ring-containing polymers is now well established. The scope of this reaction has since been extended to include a number of additional monomer types and methods of polymerization. It seemed reasonable to suppose that a suitably constructed nonconjugated dialdehyde might also be polymerized by an intra-intermolecular propagation mechanism to give polymeric cyclic acetals.

We wish to report the polymerization of glutaraldehyde to high molecular weight, soluble polymer. From the character of the polymers isolated it is concluded that the polymerization has proceeded primarily by an intra-intermolecular propagation mechanism to give a polyacetal of the general structure shown below:



$n \gg m$

The polymerization of glutaraldehyde has been effected most successfully by means of aluminum triisopropoxide catalysis at −50 to −65°C. in toluene solution. The crude product is isolated by coagulation into a nonsolvent such as hexane. Polymer yields of 12-60% have been obtained with inherent viscosities of 0.2-0.9 (0.2 g/100 ml. methylene chloride, 25°C.). The polymers are completely and reversibly soluble in common

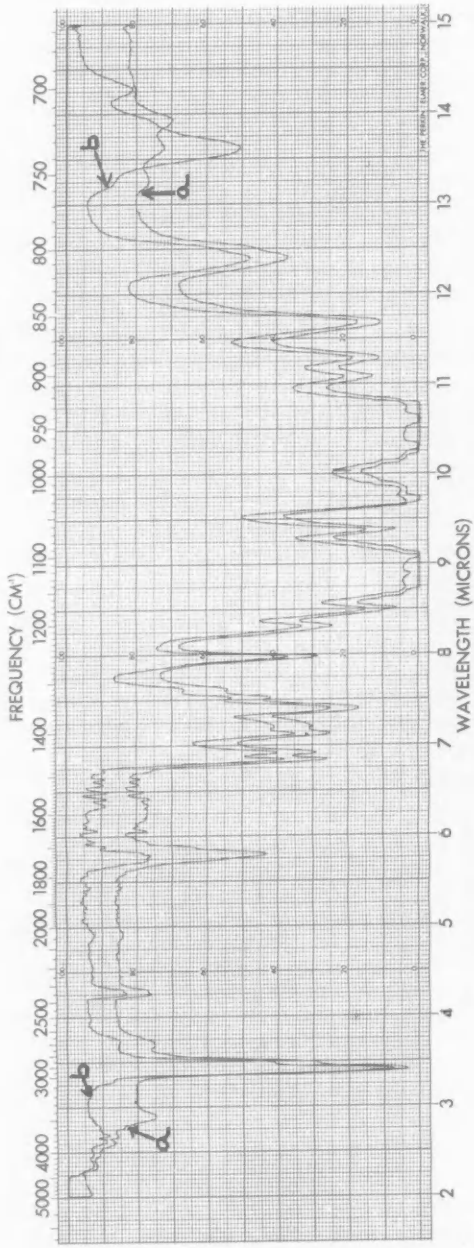


Fig. 1. Infrared spectra of polyglutaraldehyde: a. unstabilized, b. acetylated.

solvents such as methylene chloride, tetrahydrofuran, pyridine, and benzene.

Boron trifluoride-etherate in tetrahydrofuran solvent at –70°C. has also been found to be effective in polymerizing the glutaraldehyde to linear polymer. However, lower molecular weight polymer was obtained; inherent viscosity 0.2.

The white, resinous products obtained directly from the polymerization reactions are thermally unstable, as is true of all polyaldehydes. Stabilization is accomplished by esterification or etherification of the hemiacetal end groups in the manner described by Vogl (5). The stabilized polymer has a melting point of 123-133°C. (Fisher-Johns M.P. Apparatus). Clear films may be prepared by compression molding or solution casting. X-ray analysis indicates the polymer is crystalline.

Infrared spectra of polyglutaraldehyde are in good general agreement with those of other aliphatic polymonoaldehydes (6) except for a weak absorption band at 1730 $cm.^{-1}$. The complete I.R. spectra of the unstabilized (hemiacetal terminated) and stabilized (acetylated) polymer of inherent viscosity 0.9 are shown in Figure 1. The unstabilized polymer (curve a) shows a broad band at 3460 $cm.^{-1}$, characteristic of free hydroxyl groups. The acetylated polymer (curve b) has lost the hydroxyl group band but now shows an ester band at 1750 $cm.^{-1}$. The aldehyde carbonyl band, probably due to noncyclized units, remains at 1730 $cm.^{-1}$. Free monomer in the films of unstabilized polyglutaraldehyde is believed to be responsible in part for the magnitude of the adsorption band at 1730 $cm.^{-1}$ in curve a.

A more detailed discussion of this work, particularly of the polymerization catalysts and polymer structure elucidation and properties, will appear in a forthcoming publication.

Added Note: It was called to our attention that a note with related material was submitted for publication in the Journal of Polymer Science by C. G. Overberger, S. Ishida, and H. Ringsdorf, entitled: Intra-Intermolecular Polymerization of Glutaraldehyde. Professor Overberger reported briefly on his work at the Conference on "High Temperature Polymer and Fluid Research" in Dayton, Ohio, in May 1962. When hearing of our work, Professor Overberger suggested that we submit our publication.

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EQUILIBRIUM POLYMERIZATION OF SELENIUM. A RE-EVALUATION OF THE ENTHALPY OF INITIATION FROM VISCOSITY DATA

In a previous publication the ring-chain equilibrium in selenium was treated from a theoretical point of view (1), and estimates of the chain length as a function of temperature were given. The treatment was based on two equilibria: the initiation reaction, i.e., $M = M^*$ subject to the equilibrium constant K, and the propagation reaction, $M_n^* + M = M_{n+1}^*$ subject to the equilibrium constant K_3 (where M denotes the eight-membered selenium ring and the asterisk denotes a diradical). A theory which correlates the chain length with the equilibrium constants for this type of equilibrium polymerization had been developed before (2), and K_3 as a function of temperature was obtained by recalculating the data of Brieglieb (3) giving the soluble fraction of rapidly quenched liquid selenium as a function of the temperature of the liquid. It was assumed that the entropy of the ring opening reaction ΔS° in selenium was identical with that of sulfur (i.e., 23 e.u.) and finally, the enthalpy of ring opening (estimated from a comparison of bond energy values in sulfur and selenium as well as a comparison of the position of the calculated polymerization maxima and the relative separation of the viscosity-temperature curves for the two elements) was taken as 25,000 cal.

A more quantitative method developed by Gee for sulfur (4) will now be applied to the redetermination of the ΔH° for the ring opening reaction in selenium.

Gee suggested the following two equations as describing the ring-chain system of sulfur:

$$[\eta] = AP^{2/3} \tag{1}$$

$$\eta/\eta_0 = 1 + [\eta]\phi + k[\eta]^2\phi^2 \tag{2}$$

where $[\eta]$ is the intrinsic viscosity of the polymer in the monomer, P the degree of polymerization, η the viscosity of the system, η_0 the viscosity of the pure monomer, ϕ the weight fraction of polymer, and A and k constants which may depend on the temperature. The first two terms of eq. (2) were assumed to be negligible except right near the "floor temperature" of sulfur and were therefore dropped. Finally, the equation describing the viscosity of the monomer was given as:

$$-\ln \eta_0 = 9.67 - 2940/T \tag{3}$$

To adopt these three equations to the selenium system, eq. (1) and (2)

are combined omitting the first two terms of the right-hand side of eq. (2), and P and ϕ are rewritten according to the previously developed theory (2) as:

$$P = [(MoK_3 - 1)/K]^{1/2} \tag{4}$$

and

$$\phi = (Mo - M)/Mo \tag{5}$$

This yields when inserted into eq. (2):

$$\eta/\eta_0 = kA^2 [(MoK_3 - 1)/K]^{2/3} [(Mo - M)/Mo]^2 \tag{2b}$$

Due to the impossibility of obtaining data on the viscosity of pure Se_8, the temperature coefficient of the log of the viscosity of selenium is assumed to be identical to that for sulfur, but not necessarily its position, i.e.

$$\ln \eta_0 = B - 2940/T \tag{3b}$$

A combination of eqs. (2b) and (3b) yields:

$$\ln \eta = D + 2940/T + (2/3) \ln (MoK_3 - 1) + \Delta H^\circ/3T + 2 \ln [(Mo - M)/Mo] \tag{2c}$$

where D equals $\ln (kA^2) - B - \Delta S^\circ/3$ and, in the absence of data to the contrary, is assumed to be independent of temperature just as suggested by Gee for sulfur (4), at least over the narrow temperature region under consideration.

Since K_3 as a function of temperature is known from Brieglieb's solubility data and the viscosity as a function of temperature from the data of Dobinski and Wesotowski (5), one can calculate both D and ΔH° over the temperature range for which data are available. The results are $D = 10.67$ and $\Delta H^\circ = 24{,}000$ cal. This is very close to the value of $\Delta H^\circ = 25{,}000$ cal. estimated in the preceeding publication (1), the effect of this change in ΔH° is to lower log P by 0.3 units or to change P by 50%.

To check the overall self-consistency of the results, the viscosity vs. temperature curve can be duplicated over the temperature range for which data are available. The results are shown in Figure 1, calculated from eq. (2c) with $K_3 = \exp \{(\Delta S_3^\circ/R) - (\Delta H_3^\circ/RT)\}$ and $\Delta S_3^\circ = 5.47$ e.u. and $\Delta H_3^\circ = 2{,}270$ cal.

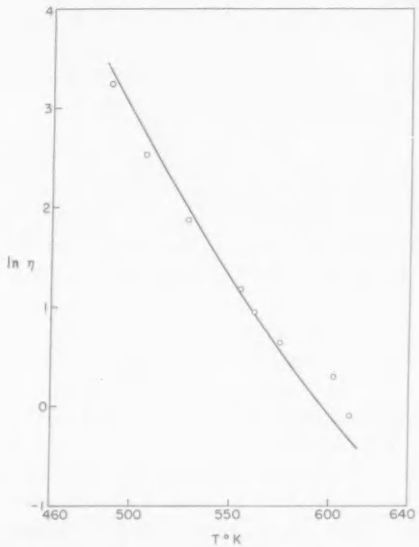

Fig. 1. Viscosity of selenium. (O) Experimental, (——) calculated.

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ELECTRON SPIN RESONANCE OF FREE RADICALS IN EPOXIDE RESINS

Jain (1) has observed electron spin resonance (e.s.r.) in commercial samples of epoxy-resin modified polyester amide polymers (Bondar), both during polymerization and during pyrolysis. As the unpolymerized sample was heated at constant temperature, the intensity of the e.s.r. absorption increased to a maximum at the gel point and then fell to zero. The resonance occurred at the free spin g-value of 2.00 and its line width was 6 to 8 gauss. The pyrolysis resonance was observed after 24 hr. heating at 250°C. and increased with time. It also occurred at g = 2.00 and had a line width of 10 to 12 gauss.

I wish to report here some observations on e.s.r. in epoxide resins. Measurements were made at room temperature with a balanced bridge superheterodyne spectrometer operating at 9000 Mcycles/sec. with derivative presentation of the spectrum on a chart recorder. The epoxide samples were prepared as 5 mm. diameter rods which were inserted along the axis of a cylindrical TE_{011} microwave resonator. Immediately after curing, all rods showed a symmetrical e.s.r. absorption with $g = 2.006 \pm 0.001$ and a line width $\Delta H_{ms} = 10 \pm 1$ gauss. The intensity of the resonance varied from one batch of rods to another, but was essentially constant within a given batch. The concentration of free radicals in one batch of five rods was estimated by comparison with a standard sample of Mn^{2+} ions in zinc sulfide to be 1.6×10^{-6}m. Two rods were heated in air to 180°C. and their resonances were compared periodically with those of the unheated rods. Throughout these tests, the resonances of the unheated rods remained unchanged in intensity, line width, and g-factor. The intensities of the resonances of the heated rods changed as shown in Table I. The line widths of the resonances decreased from the initial value of 10 gauss to 8 gauss after twelve days heating and 7 gauss after 19 days heating. The g-values of the resonances remained unchanged. The intensities of the resonances of the heated rods do not show a steady increase or decrease. The two sets of results show very similar variations and suggest that both production and decay of the radicals were occurring simultaneously, and that the relative rates of these processes were determined by some factor which was essentially the same for both rods, but which varied from one heating period to the next, such as the exact temperature of the rods. Immediately after the curing process, the epoxide rods were light yellow in color and during the heating, they progressively darkened. In thick blocks of resin, this effect is observed near the surface only, and is probably due to diffusion controlled oxidation.

TABLE I.

Total heating time in days	Relative e.s.r. intensity	
	Sample A	Sample B
0	1.0	1.0
1	0.4	0.5
2	0.3	0.3
3	0.7	0.9
4	0.7	0.7
5	0.3	0.3
12	2.4	2.8
19	0.8	0.8

To investigate the effect of air on the pyrolysis, two rods were placed in quartz tubes and sealed off under high vacuum. Before heating, both rods had e.s.r. absorptions with g-values and line widths identical to those of the first set of rods, and with intensities about 20% higher. After heating for 24 hr. no e.s.r. absorption was detected and both rods had become lighter in color than the unheated rods. On further heating in vacuum, no e.s.r. absorption was produced and the rods remained unchanged in color.

Free radicals produced in polymers are usually unstable and disappear if the polymer is heated to a temperature at which molecular diffusion can take place. The diffusion of oxygen into polymers containing free radicals usually has one or both of two effects: The radicals may disappear without being replaced by other paramagnetic species, or they may be replaced by an asymmetric resonance which has been attributed to peroxy radicals, the asymmetry arising from anisotropy in the g-factor of the resonance (2-4).

The disappearance of the radicals on heating the epoxide rods in vacuum shows that this process occurs through molecular diffusion, rather than through interaction with oxygen. On the other hand, diffusion of air into the samples is necessary for radical production. The darkening and the radical production are probably related.

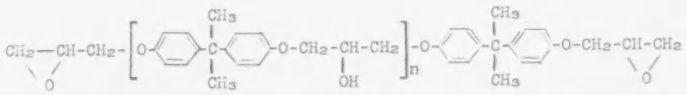
The g-factor of 2.006 is only slightly larger than the free-spin value of 2.0023 and the orbital contribution to the paramagnetism is very small. From this, and the width and symmetry of the resonance, the presence of peroxy radicals can immediately be discounted. Radicals of the type $RO^{\cdot}$, where R is aliphatic, can similarly be ruled out (5,6).

Further conclusions can be drawn from the absence of structure, and from the line width of the resonance. Aliphatic radicals, having the unpaired electron located mainly on a particular carbon atom, give hyperfine patterns arising from interactions between the unpaired electron and α and β protons. A single interacting proton will split the resonance in-

to a doublet separated by about 20 gauss. Wider and more complex patterns are given by larger numbers of interacting protons. If many different aliphatic radicals were present, resolution of the individual lines would be lost, but the line width would be much greater than the observed 10 gauss.

One possibility is that the unpaired electrons are not located on particular atoms, but can move over several atoms, as in the π-molecular orbital system of an aromatic molecule. The proton hyperfine interactions would then be reduced owing to the reduction of spin density on the individual carbon atoms.

The basic reaction in the formation of these resins is the condensation of Bisphenol A with epichlorohydrin to give a polymer of typical structure:



Crosslinking (not shown above) occurs both during preparation of the resin and during the curing process. It is suggested that the unpaired electrons are associated with the benzene rings. It is probable that oxidative scission of the polymer chains takes place close to a benzene ring, to give a radical such as:

Either of these radicals would give spectra of the type observed.

It is concluded that, when epoxy resins are heated to 180°C. in air, both formation and decay of free radicals occur. In vacuum, the decay alone takes place and is due to a diffusion controlled interaction between the radicals. Formation of the radicals requires the presence of air and probably involves an oxidative scission of the polymer chains. The radicals observed are probably of the semiquinone or aryloxy type rather than aliphatic or alkyl radicals, peroxy, or alkoxy radicals. The slight narrowing of the resonance with time of heating suggests a change in the detailed structure of the radicals as heating continues. It is concluded that, at least in the early stages, attack of oxygen on the polymer chains plays an important role in the thermal ageing process.

I wish to thank Dr. K. A. Muller and M. Pierre Burnier for suggesting this problem and for many helpful discussions.

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ELECTRON TRANSFER REACTIONS AND THE FORMATION OF POLYRADICALANIONS

Biphenyl forms a blue radicalanion complex with alkali metals. This reaction takes place readily in ether-type solvents and involves electron transfer from the metal to the π electron orbitals of the biphenyl (1). Our studies showed that the biphenyl moieties in poly-4-vinylbiphenyl (PVB) undergo the same reaction: we propose to refer to this and other polymers containing radicalanions distributed along the chain as polyradicalanions. We have found also that 4-vinylbiphenyl in THF reacts with sodium to yield a red-colored polymeric "living" anion. This anion will polymerize additional vinylbiphenyl as well as other vinyl monomers.

When PVB in THF was placed over sodium, a blue color identical to that of the biphenyl radicalanion was formed. The color disappeared on addition of methanol, but after isolating and redissolving the polymer, the color reappeared upon addition of fresh sodium. Following the same sequence the color could be regenerated a few times. Since methanol destroys the radicalanion by converting an aromatic ring to a dihydro derivative, these observations imply that each time sodium reacts with an additional portion of the biphenyl moieties. Titrations of the sodium bound to the polymer showed that, under the experimental conditions used, ca. 30% of the total biphenyl could be complexed. ESR spectra demonstrated the presence of unpaired electrons in concentrations proportional to the sodium content.

The visible spectrum of the polyradicalanion exhibits absorption bands at 400 and 600 mμ, the same regions in which the biphenyl complex absorbs; the polymer anion has a band in the 480 mμ region. The polyradicalanion spectrum is stable at –80°C., but at room temperature gradually changes into that of the anion as shown in Figure 1. Since the increase in anion content means an increase in the number of chain-ends, these changes in the spectrum indicate chain scission reactions.

The occurrence of degradation was ascertained following over a six-day period the viscosity changes in two aliquots of a polyradicalanion solution in THF kept at 25 and 50°C., respectively (Fig. 2). The same asymptotic viscosity value was reached for both temperatures. The observed changes correspond to a decrease in $(DP)_n$ from about 1200 to 300, and indicate an average of three scissions per chain. Having started with 60 radicalanion units (by sodium analysis) and assuming random distribution along the chain, there should be on the average three configurations per chain in which two adjacent biphenyls are complexed. As this number coincides with the number of scissions, it suggests that the instability of the chain is due to doublet configurations. Additional

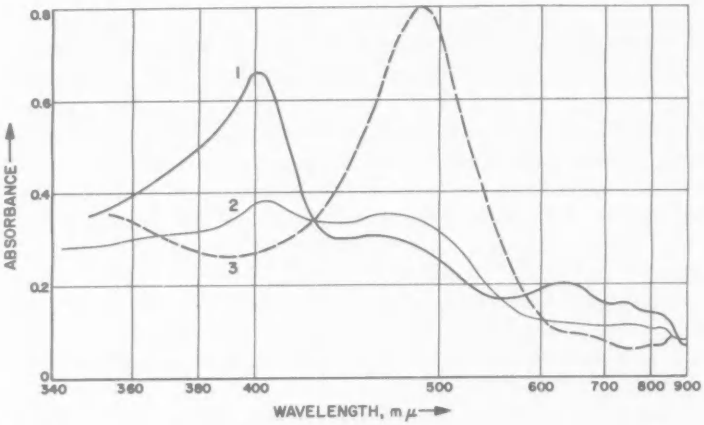


Fig. 1. Visible spectra of PVB polyradicalanion after 6 hr. (1), after 3 days at room temperature (2), and PVB dianion (3).

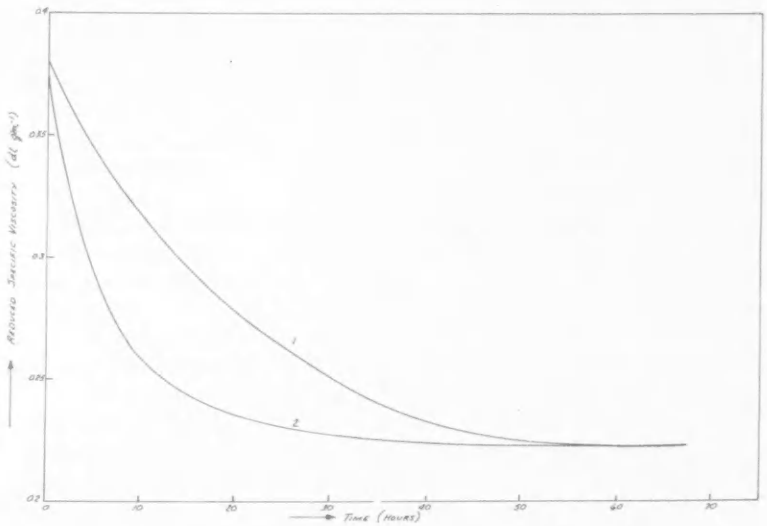


Fig. 2. Effect of temperature on the degradation of poly-4-vinylbiphenyl at the same sodium concentration (7.2 millimoles /liter). Reduced specific viscosity at (1) 25°C. and (2) 50°C.

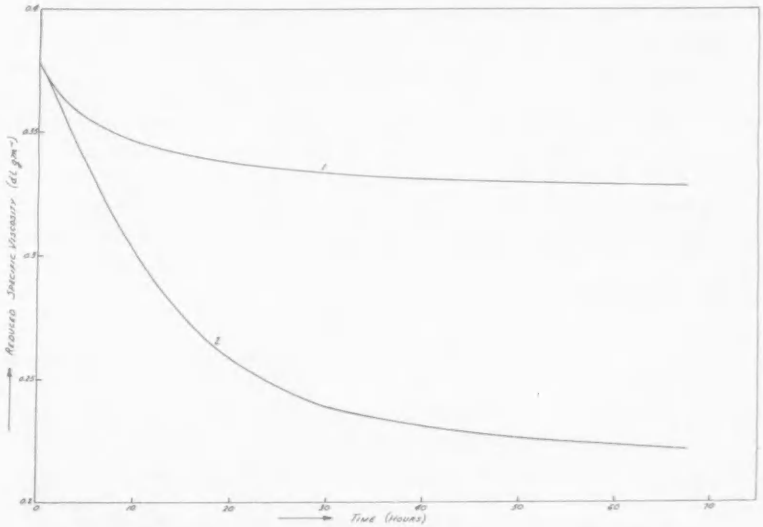
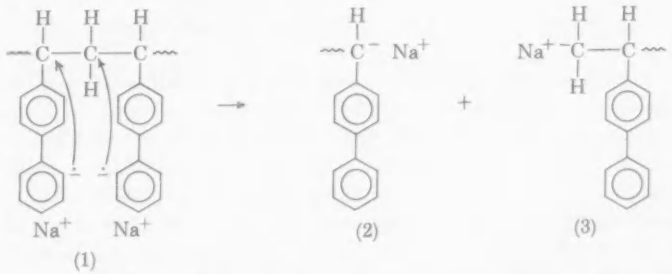


Fig. 3. Effect of sodium concentration on the degradation of poly-4-vinylbiphenyl. (1) 2.5 millimoles and (2) 7.4 millimoles of Na/liter.

viscosity studies showed that the ultimate extent of degradation could be correlated with the sodium content and was found to be independent of temperature (Fig. 3). In contrast to the polyradicalanion, the "living" anion solution viscosities remained unchanged for 18 hr. at 60°C. Analysis of the available data indicates that the first-order kinetics describe the degradation process.

The bond dissociation is probably caused by electron migration from the aromatic rings to the α-carbon of the aliphatic chain. The following mechanism is suggested:



The existence of species (2) has been proved spectroscopically (Fig. 1),

TABLE I

π-Resonance Energy Gain after Bond Scission

Polymer	Energy gain in units of β
Polyvinylanthracene	1.7800
Poly-β-vinylnaphthalene	1.9798
Poly-α-vinylnaphthalene	2.0484
Poly-4-vinylbiphenyl	2.1655
Polystyrene	2.7206
Polyacenaphthylene	2.8608

and species (3) is expected to be an unstable intermediate which should rearrange.

Consideration of the π-resonance energy differences between radical-anion doublets and the resulting anions show the postulated C-C bond dissociation to be energetically favorable. These energies, calculated by the Hueckel-molecular-orbital approximation for the species investigated are listed in Table I in order of increased resonance gains. If this energy gain is the main factor determining the tendency for bond scission, then Table I provides a relative stability scale for the radical-anions. These considerations are consistent with experimental results (2). The same mechanism and criterion for stability should apply in general to the dissociation of a C-C bond by an alkali metal reported for hydrocarbons such as $\phi_2CH–CH\phi_2$ (3).

Reactive sites distributed along the polyradicalanion chain offer possibilities for chemical modifications of the polymer. Lithium, sodium, and cesium complexes of PVB in THF solution all reacted readily with CO_2 at temperatures below 0°C. to form carboxylic acids. Results of elemental analysis on the polymeric reaction products showed that ca. 30% of the biphenyl could be reacted with CO_2. In the IR absorption bands appeared at 5.85 and 7.8 μ. These bands are characteristic of the carbonyl, and the coupled CO-OH in-plane deformation modes, respectively (4).

The PVB-sodium complex initiated the polymerization of styrene, isoprene, α-vinylnaphthalene, and ethylene oxide. By analogy to the polymerization with the sodium-naphthalene complex (5), one should expect the latter to form a bond with the radicalanion initiator. Thus, with ethylene oxide graft polymers were obtained. Direct evidence for bond formation was obtained from spectroscopic and solubility studies on polyoxyethylene initiated by the biphenyl-cesium complex. The appearance of an absorption band at 225-231 mμ could be attributed to the modification of the biphenyl molecule due to bond formation.

Our studies on intra-molecular electron transfer reactions have included polymers of α- and β-vinylnaphthalene, 9-vinylanthracene, and acenaphthylene (6). The general pattern of behavior is similar to that of PVB. The polyacenaphthylene complex was found to undergo bond scission with extreme ease in accordance with the resonance energy calculations (Table I). The latter indicate that polyradicalanions of polystyrene should also be very unstable. Preliminary experiments show that this is indeed the case.

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AN X-RAY EXAMINATION OF POLY-O-ACETYL-L-SERINE

An oriented film of poly-O-acetyl-L-serine (with mean degree of polymerization of about 80) has been obtained from its trifluoroacetic-acid solution. The film shows a marked positive birefringence, i.e., it shows a higher refractive index with the electric vector of the visible light parallel to the direction of the orientation (fiber axis) than that with the electric vector perpendicular to the fiber axis. Of this film, x-ray fiber diagrams have been obtained by the use of the Ni-filtered Cu radiation and a cylindrical (radius = 28.65 mm.) camera. One of the diagrams obtained with the incident x-ray beam placed in the plane of the film and perpendicular to the fiber axis is reproduced in Figure 1.

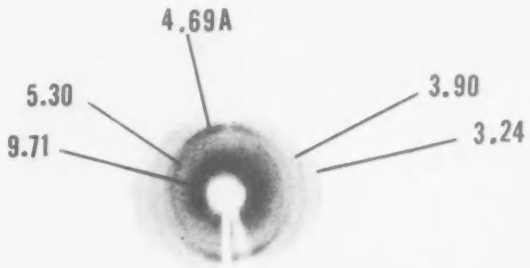

Fig. 1. X-ray diffraction photograph (x1) of an oriented film of poly-O-acetyl-L-serine obtained by the use of Ni-filtered Cu radiation. The x-ray beam was placed in the plane of the film and perpendicular to the fiber axis.

As may be seen in the figure, five reflection arcs are observed with the Bragg spacings of 9.71, 5.30, 4.69, 3.90, and 3.24 A. The intensities of these reflections are listed in Table I. The length of the reflection arcs are fairly great, probably because the degree of orientation of the fibers in the film is not high. It is clear, however, that the centers of the 9.71 and 3.24 A. reflections are located on the equatorial line. The strong reflection of 4.69 A. seems to be on the meridian. The center of the 3.90 A. reflection arc seems to be on a layer line with the $1/\zeta$ value of about 4.8 A., and that of the 5.30 A. seems to be on another layer line with the $1/\zeta$ value of about 9 A. (ζ is the coordinate along the fiber

axis in the reciprocal space.)

All five reflections may be indexed with an orthorhombic cell with a = 9.6 A. (fiber axis), b = 6.48 A., and c = 9.71 A. (see Table I).

TABLE I

Observed Reflections

Bragg spacing, A.	Relative intensity	Index
9.71	30	001
5.30	5	110
4.69	10	200
3.90	2	210
3.24	3	020

The appearance of the strong reflection of 4.69 A. on the meridian suggests that the structure of poly-O-acetyl-L-serine film in question is of the cross-β type (7). This spacing corresponds approximately to the distance between two extended polypeptide chains linked by the C=O... H–N hydrogen bonds. The cross-β structure of this polymer has been suggested from a study of infrared absorptions (2). The structure may also be suggested from the positive birefringence of the film mentioned above. The spacing of 3.24 A. of the equatrial reflection may correspond to one half of the length (6.48 A.) of the repeating unit along the nearly extended zigzag chain. The repeating distance of 6.48 A. is slightly less than, but almost equal to, what is expected for antiparallel-chain pleated sheet (3). The fact that the strong meridional reflection of 4.69 A. mentioned above appears apparently on the second layer also suggests that the two adjacent chains are antiparallel to each other. Thus, if the chains were parallel, the 4.69 A. should be the true repeating distance along the fiber axis. While, if they are antiparallel, the true repeating distance would be twice 4.69 A. The strong equatorial reflection of 9.71 A. is considered to correspond to the distance between consecutive sheets (the side-chain spacing). This is much shorter than the side-chain spacing (12.5 A.) of poly-β-n-propyl-L-asparatate (1) in its cross-β form. This difference in the side-chain spacings is to be related to the difference in the side-chain lengths of poly-O-acetyl-L-serine and poly-β-n-propyl-L-asparatate.

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SINGLE POLYOXYMETHYLENE CRYSTALS BY SOLID STATE POLYMERIZATION OF TRIOXANE

Recently several publications have shown that trioxane polymerization can be induced by radiation (1) and by cationic catalysts (2). Starting with large trioxane crystals, polyoxymethylene samples of excellent orientation as observed by x-ray diffraction were obtained (1,2).

In our work, trioxane crystal needles were polymerized with BF_3 gas at room temperature and unreacted trioxane carefully removed with acetone. Usually, because of the large size of the original trioxane crystals, hollow needles of polymer were obtained, indicating that polymerization progressed gradually from the outside (2).

A detailed x-ray diffraction examination of a small section of such a crystal (some of the needles were several centimeters long) indicated the following:

The polyoxymethylene chains lie almost exclusively in the direction of the c-axis of the trioxane crystal, since a perfect fiber diagram is obtained with the c-axis of the polymer in the original needle direction (c-axis of trioxane) (5). Weissenberg and precession photographs show that in these crystals there exists excellent three-dimensional order, that is, the crystals are not only oriented with respect to the fiber axis (uniaxial orientation), they also have specific lateral axis directions. In the samples investigated, the a-axis direction was perpendicular to the needle surface.

The sharpness and the number of the diffraction spots (Tables I-III, Figs. 1 and 2) indicate a considerably larger size and perfection of these crystals than has been obtained in fiber diagrams of highly oriented and annealed fibers (3). Especially evident is the complete absence of amorphous scattering that is usually noted in polyoxymethylene diagrams (3).

The unit cell dimensions of the hexagonal cell, a = 4.50 A., c = 17.35 A., agree with those reported by Sauter (4). The very strong 3.9 A. spacing observed in radiation-induced polymer (1) is only visible weakly and in some crystals is practically completely absent. Hayashi (1) ascribes these diffraction spots to polyoxymethylene crystals growing along a diagonal direction of the trioxane crystal. The few spots visible on our rotation and oscillation photographs may also originate from a different crystal structure (6) of lower symmetry than the Sauter (4) structure, with its c-axis about 14.0 A. long and coinciding with the c-axis of the trioxane crystal. The difference in intensity and therefore concentration of the two polyoxymethylene structures may indicate differences in polymerization mechanisms of the radiation-induced (1) and BF_3 vapor-initiated processes.

TABLE I

Spacing and Intensity of the Observed Diffraction Spots of a Rotation Diagram of Polyoxymethylene Single Crystal (Rotation Axis: c-Axis)*

l	hk = 10 d* = .395	11 .685	20 .790	21 1.055	30 1.190	22 1.375	31 1.430	32 1.730	41 1.820
Equator	v.s.	s.	w.	m.	m.–	w.	m.–	w.	–
1st layer	–	w.	w.	w.	–	–	–	–	–
2nd layer	–	–	–	v.w.	–	?	?	–	–
3rd layer	w.	m.	m.	m.	w.	v.w.	w.	v.w.	–
4th layer	w.+	m.+	m.+	w.	–	–	–	–	–
5th layer	v.s.	v.s.	v.s.	m.+	w.	?	?	v.w.	v.w.
6th layer	–	–	–	–	–	–	–	–	–
7th layer	–	–	–	–	–	–	–	–	–
8th layer	s.	s.	s.–	m.+	w.	v.w.	v.w.	–	–
9th layer	s.	v.w.	–	–	–	–	–	–	–
10th layer	–	w.	w.	–	w.	–	–	–	–

*Ni-filtered CuKα radiation, cylindrical camera (Unicam) 30 mm. radius. (See Fig. 1).

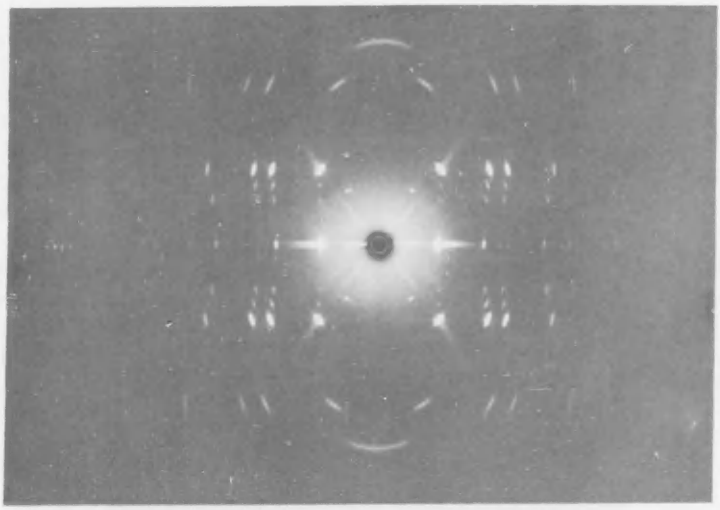

Fig. 1. Rotation photograph of polyoxymethylene crystal, (rotation axis, needle (c) axis of trioxane. Unicam cylindrical camera, 30 mm. radius CuKα radiation, Ni-filter).

TABLE II

Weissenberg Zero Layer and Fifth Layer Intensities

d,A.	Int.	Zero layer hko
3.96	v.s.	10, $1\bar{1}$, $0\bar{1}$, $\bar{1}0$
2.28	m.	11, $2\bar{1}$, $1\bar{2}$, $\bar{1}\bar{1}$
1.98	v.w.	20, $2\bar{2}$, $0\bar{2}$
1.50	w.	12, 21, $3\bar{1}$, $3\bar{2}$, $2\bar{3}$, $1\bar{3}$, $\bar{1}2$
1.32	w.	30, $3\bar{3}$, $0\bar{3}$
1.14	w.	22, $4\bar{2}$, $2\bar{4}$
1.09	w.	13, 31, $4\bar{1}$, $4\bar{3}$, $3\bar{4}$, $1\bar{4}$, $\bar{1}\bar{3}$
		Fifth layer hk5
3.87	v.v.s.	10, $1\bar{1}$, $0\bar{1}$
2.22	v.s.	11, $2\bar{1}$, $1\bar{2}$, $\bar{1}\bar{1}$
1.92	s.	20, $2\bar{2}$, $0\bar{2}$
1.45	w.	12, 21, $3\bar{1}$, $3\bar{2}$, $2\bar{3}$, $1\bar{3}$, $\bar{1}2$
1.28	v.w.	30, $3\bar{3}$, $0\bar{3}$

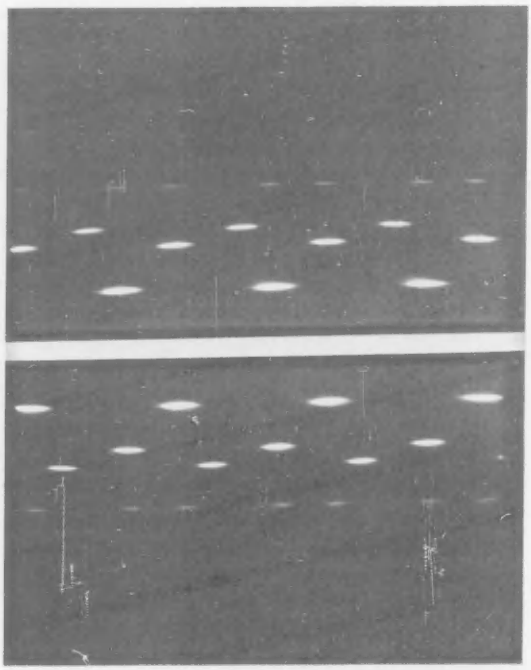

Fig. 2. Equi-inclination Weissenberg photograph, hk5 plane, (Van der Heyde Weissenberg camera 57.3 mm. diameter CuKα radiation Ni-filter).

TABLE III

Precession Photograph of ac Plane, X-Ray Beam Parallel to Needle Surface (Filtered MoKα Radiation)

hol	Int.	hol	Int.
009	m.$^+$	205	m.
00,18	m.$^+$	208	w.
100	v.s.	20,10	w.
105	s.	20,13	w.
108	w.	300	v.w.
109	w.?		
10,13	m.$^-$	c spacing = 17.31 A.	
10.18	w.$^+$	a spacing = 4.50 A.	

While the x-ray diffraction photographs reveal remarkably perfect, three dimensionally ordered polymer crystals, both orientation and perfection are still not equal to that of the original trioxane or other low molecular single crystals.

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NOTES ON NYLON 6 SINGLE CRYSTAL

It was confirmed by Geil that poly-ϵ-caproamide (nylon 6) could crystallize as a single crystal (1). From measurement of the selected-area electron diffraction, he assumed that nylon 6 single crystals might have a high temperature crystal modification such as that proposed by Hutino and Okada (2).

We suggest instead that it may be interpreted more definitely in terms of another crystal modification (γ-form) of nylon 6, whose occurrence has been indicated mainly by Japanese investigators (3-5). It is obtained by treatment of nylon 6 with iodine-potassium iodide solution with subsequent removal of iodine with sodium thiosulfate. Recently we found that the γ-form crystal could be detected even in the film made from the formic acid polymer solution, and we determined its crystal structure (6).

In the selected-area electron diffraction pattern of the nylon single crystal obtained in this laboratory by the same procedure as that adopted by Geil (Figs. 1 and 2), we observed many sharp diffraction spots up to the higher order of reflection with spacing of 1.0 A.

This means that it may have a much more perfect crystalline structure than was supposed for the one whose molecular chain packing is axially symmetrical so that the hydrogen bonds is randomly oriented. According to our x-ray analysis, the γ-form has the structure whose cell dimensions are

$$a = 9.35 \text{ A.}, \quad b = 16.60 \text{ A. (fiber axis)}, \quad c = 4.81 \text{ A.}, \quad \beta = 120^\circ$$

Fig. 1. The electron micrograph of a nylon 6 single crystal.

Fig. 2. The selected area electron diffraction pattern of a nylon 6 single crystal.

and has the space group of $C_{2h}^5 - P2_1/a$.

The most important difference of this form from the well-known crystal structures (α and β by Bunn's notation) is that hydrogen bonds are formed not between the antiparallel chains as in the latter, but between the parallel ones.

When the structure of the γ-form determined by us is adopted, the four of the six innermost spots with spacing of 4.1 A. and the two with spacing of 4.0 A. will be assigned reflections of the plane of [(001), ($\bar{2}$01)] and [(200)], respectively, and the remaining ones equatorial reflections. These assignments can satisfy the extinction law of the reflections

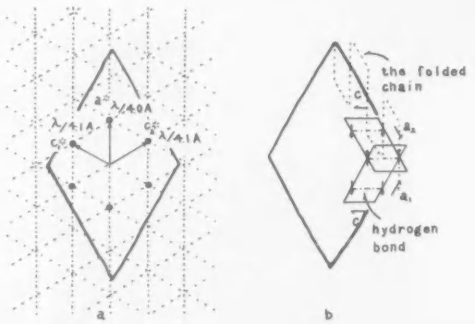

Fig. 3. The schematic representation of the crystalline structure of the single crystal in terms of the reciprocal lattice (Fig. 3a) and the real lattice of the γ-form (Fig. 3b). The arrows (↑) show the chain direction.

Fig 4. The electron micrograph of a cleaved nylon 6 single crystal produced by virtue of ultrasonic wave.

(h0l) up to the order of h = 8.

The above relation is represented by the reciprocal lattice written at the surface of the single crystal (Fig. 3a), where the a*-axis coincides with the observed direction of the major axis of the lozenge.

The real lattice transformed from it is shown in Figure 3b, where the c- and a-axis (a_1- and a_2-) are directed respectively to the minor axis and the side, and the b-axis is perpendicular to the surface of the single crystal.

In this case, it should be noticed that hydrogen bonds are formed between the parallel segments belonging to the different folded chains and that they have a specified direction parallel to the minor axis of the lozenge-like single crystal.

This conclusion will be supported by further observation of the electron micrographs of the single crystal which underwent mechanical force to produce local cleavage. They are shown by Figures 4 and 5, which were taken of a suspension of nylon 6 in glycerine that was subjected beforehand to ultrasonic waves of 8×10^5 cycles/sec. for 30 min. at room temperature (7).

Two kinds of crack can be noticed in Figure 4; the one with "fibrillar" material occurred along the direction of the minor axis and the other along the side. Figure 5 shows the wider crack fortuitously produced by simultaneous cleavage of the substrate film. The "fibrillar" material seems to have been formed by the polymer chains which were unfolded by elongation of the single crystal along the direction of the major axis.

If this occurs, it will have a fiber structure similar to that in the drawn fiber. Although the electron diffraction pattern in this area is not

Fig. 5. The electron micrograph of a nylon 6 single crystal cleaved with formation of the "fibrillar" material.

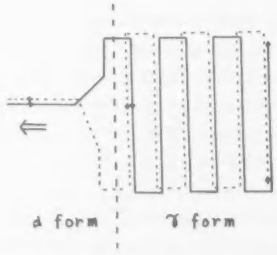

Fig. 6. The projection of the folded chains to the surface perpendicular to the minor axis.

yet been taken with success, it has been demonstrated by us that the γ-form crystal undergoes an easy change of the γ-α transformation when the original specimen film is stretched. It is very probable that the intrinsic difference in the character of hydrogen bond formation between the γ- and α- (or β-) crystal would restrict the arrangement of the folded chains in the nylon 6 single crystal. Figure 6 shows one possible way for chain packing.

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(7) To obtain the electron micrograph of torn sign single crystals of polyethylene, Hirai et al. employed the same procedure as ours. H. Hirai, H. Kiso, and T. Yasui, Chem. High Polymers, Japan, 19, 46 (1962).

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POLYMER NEWS

The Winter Gordon Research Conference on Polymers will be held at the Hotel Miramar, Santa Barbara, California, February 4-8, 1963. Robert Simha will be the Chairman, and Maurice L. Huggins will be the Vice Chairman. The program is as follows:

February 4: J. R. Van Wazer, "Random and non-random reorganization, including functionality changes; application to inorganic systems;" C. A. Klein, "Crystal structure and physical properties of pyrolytic graphites;" L. A. Wall, "Some remarks on high temperature polymers."

February 5: J. D. Ferry, "The role of free volume in the dependence of viscoelastic properties on molecular weight distribution and in time-dependent viscoelastic properties near the glass transition temperature;" T. G. Fox, "Free volume, chain entanglements and the properties of concentrated polymer systems."

February 6: J. Vinograd, "Equilibrium sedimentation of biological macromolecules in a density gradient;" J. J. Hermans, "Application of density gradient centrifugation to synthetic polymers;" R. L. Baldwin, "Physical chemistry of synthetic DNA's."

February 7: B. H. Zimm, "Theory of uncoiling of DNA molecules;" E. P. Geiduschek, "Physico-chemical and biological properties of crosslinked DNA molecules;" H. F. Mark, "Recent progress in polymer research." Business session.

February 8: "Contributions on recent research."

A one-day institute entitled "Polymers as Engineering Materials" will be conducted Thursday, February 7, at Newark College of Engineering, Newark, N. J., from 9:30 a.m. to 4:30 p.m. in the college's Weston Hall, 367 High St. The registration fee, including luncheon, is $10 per person.

Requests for registration cards should be directed to Professor Stephans, Office of Relations with Industry, Newark College of Engineering, 323 High St., Newark 2, N. J.

Following is a list of the speakers and synopses of their talks:

Fibers: Dr. Emerson A. Tippetts, Relationships between the chemical structures of polymers and the physical structures which are possible therefrom. Fiber properties will be treated in terms of both chemical and physical structure.

Coatings: Gene L. Leithauser, Influence of polymer structure and resin composition as related to the properties of organic coatings. Included will be the selection of polymers for specific coating applications.

Adhesives: Dr. Joseph F. Abere, Development of adhesion between two surfaces in terms of molecular structure, polar group interaction, mechanical surface characteristics, and development of chemical bonds. Adhesion will be related to polymer structures and their associated surface energies.

Elastomers: Dr. Maurice Morton, Elastomeric polymers in light of the theories of rubber elasticity. Included will be the structural requirements of the polymer chain which are necessary for elastic behavior.

Plastics: Dr. Herman S. Kaufman, The chemical and structural characteristics of polymers as they may be related to plastic properties, and the interrelationships between fabrication techniques of plastics and their physical properties and structures.

Manuscripts should be submitted to one of the members of the Editorial Board or to the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn 1, New York. Address all other correspondence to Interscience Publishers, a Division of John Wiley & Sons, Inc., 440 Park Avenue South, New York 16, New York.